Microwave-assisted Synthesis of Single-crystalline CuO Nanoleaves

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Single-crystalline CuO nanoleaves with an average thickness of about 10 nm and with lateral sizes of hundreds of nanometers to several micrometers have been successfully synthesized by microwave-heating of an aqueous solution containing copper salt and sodium hydroxide. CuO nanoleaves were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and UV–vis absorption spectrum. The band gap of CuO nanoleaves was estimated to be $\approx$2.13 eV, which shows significant blue-shift compared with that of the bulk.

CuO is a p-type semiconductor with a narrow band gap (1.21 eV). CuO has attracted considerable attention due to its wide range of applications. It has been studied extensively as a component of high-T_c copper oxide superconductors[1,2] and promising material for fabricating solar cells and lithium ion battery.[3] CuO is also widely used in applications such as catalyst[4] and gas sensors.[5,6] Recently, different methods for synthesis of CuO nanoparticles[7–11] and nanorods/nanowires[12–19] have been reported.

Since the first reports of microwave-assisted liquid phase organic synthesis in 1986,[20,21] the application of microwave heating in synthetic chemistry has been a fast growing area of research. Compared with conventional heating methods, microwave heating has been accepted as a promising method for rapid volumetric heating, higher reaction rates, and shorter reaction times. As a result, this has opened up the possibility of realizing fast synthesis of nanomaterials in a very short time.[22]

In this paper, we demonstrate that single-crystalline CuO nanoleaves can be synthesized via a microwave-assisted aqueous solution method. This method is a fast, simple, seedless, and template-free route for production of CuO nanoleaves.

$Cu(CH_3COO)_2 \cdot H_2O$ (analytical grade (AR)), $CuCl_2 \cdot 2H_2O$ (AR) and sodium dodecylsulfate (SDS, chemical purity (CP)) were purchased from China Medicine Group Shanghai Chemical Reagents Company. NaOH (AR) and $NH_3 \cdot H_2O$ (AR) were purchased from Shanghai LingFeng Chemical Reagents Co. Ltd. All the solutions were prepared using deionized water as the solvent. The procedure for the synthesis of sample 1 is as follows: 4 mL of 0.1 M NaOH solution was added dropwise to 52 mL of 3.85×10^{-3} M $Cu(CH_3COO)_2$ solution under magnetic stirring. Then 0.2 mL of 0.1 M SDS solution was added to the above solution. The resulting solution was microwave-heated to boiling point and held at this temperature for 20 min. Sample 2 was prepared as follows: 6 M $NH_3 \cdot H_2O$ was added dropwise to 22 mL of 9.1×10^{-3} M $CuCl_2$ solution until the blue precipitate dissolved completely. Then 0.5 mL of 6 M NaOH solution was added dropwise under magnetic stirring. The resulting solution was microwave-heated to 80 °C and held at that temperature for

10 min. The microwave oven (2.45 GHz, maximum power 300 W) used was a focused single-mode microwave synthesis system (Discover, CEM, USA). Temperature was accurately controlled by automatic adjusting of microwave power. The microwave synthesis system was equipped with a water-cooled condenser outside the microwave cavity and a magnetic stirring system. After the solutions cooled to room temperature, the products were centrifuged and washed with deionized water three times and with absolute ethanol one time. Finally the products were dried in a vacuum at 60 °C.

XRD patterns were recorded on a Huber G 670 diffractometer using graphite-monochromatized high-intensity Cu Kα_1 radiation. TEM images were obtained on JEOL JEM-2010 transmission electron microscope. The UV–vis absorption spectra were recorded by Shimadzu UV-3101 scanning photospectrometer.

The XRD pattern of sample 1 is shown in Figure 1, which shows the single phase of CuO with the monoclinic structure (JCPDS 80-1917).
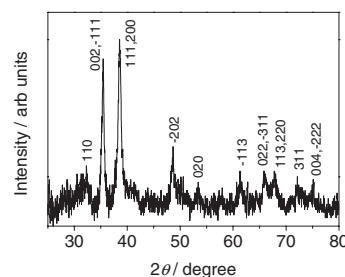

Figure 1. The XRD pattern of sample 1.

The morphologies of the as-prepared CuO samples were studied by TEM. Figures 2a and 2b show the TEM micrographs of sample 1, from which one can see leaf-like nanosheets (nanoleaves) with widths in the range of 160–280 nm and lengths in the range of 1.5–2.8 μm. It is interesting that the ratio of length to width for most CuO nanoleaves is $\approx$10. In some cases, branched tips were observed (see Figure 2a labeled with circles). Figures 2c and 2d show the TEM images of sample 2. The CuO crystals also have the leaf-shaped morphology with widths in the range of 540–660 nm and lengths in the range of 2–2.5 μm. The ratio of length to width is $\approx$4. The estimated thickness of CuO nanoleaves is $\approx$10 nm based on the observation of the nanoleaves standing on the carbon film of TEM copper grid. Some broken nanoleaves were found in these two samples, indicating that the CuO nanoleaves were thin and fragile.

The SAED patterns in Figures 2b and 2d were taken from a single nanoleaf from samples 1 and 2, respectively, by focusing the electron beam along the [001] direction. Both patterns can be indexed to the reflections of the monoclinic CuO structure,

which is consistent with the result obtained from XRD. SAED patterns obtained from different individual CuO nanoleaves in these samples were essentially the same, indicating the single-crystalline nanoleaves with the surfaces parallel to (001) plane of the monoclinic CuO.
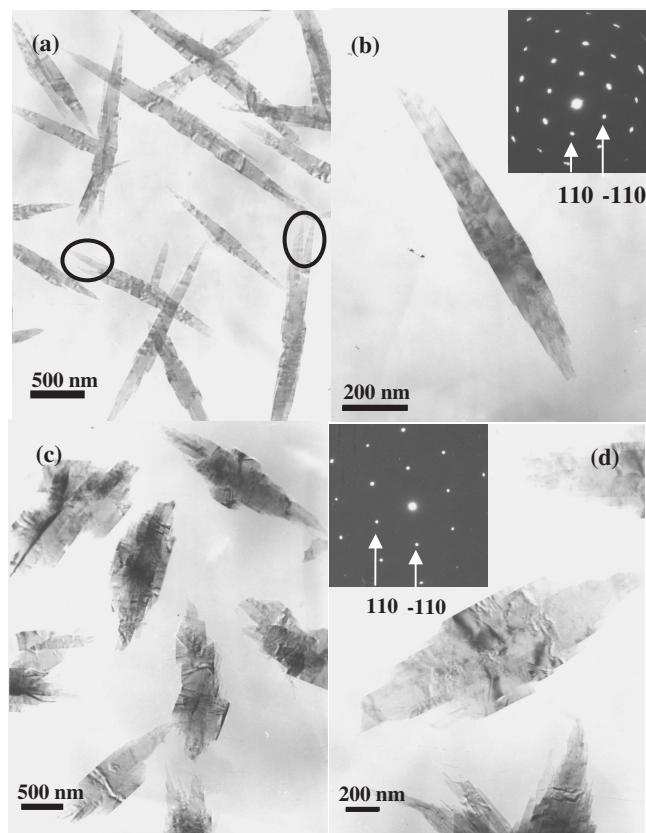

Figure 2. TEM micrographs of CuO nanoleaves. (a) and (b) sample 1; (c) and (d) sample 2.

Our experiments showed that the concentration of SDS had little effect on the morphology and size of the product in the range of 10^{-3}–10^{-5} M. The sequence of addition of SDS and NaOH to the solution has an effect on the morphology of the product. If SDS was added to the solution before the addition of NaOH, the product consisted mainly of irregularly shaped particles. We also studied the influence of the copper source on the morphology of CuO. The copper source ($Cu(CH_3COO)_2$ and $CuCl_2$) had a little influence on the morphology of the product.

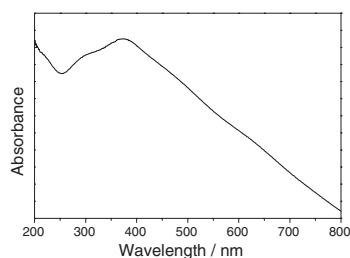We have studied the UV–vis absorption of the product in

Figure 3. UV–vis absorption spectrum of sample 1 dispersed in absolute ethanol.

order to resolve the excitonic or interband transitions of CuO nanoleaves. Figure 3 shows the UV–vis absorption spectrum of sample 1 dispersed in absolute ethanol. The spectrum shows a broad absorption peak at about 375 nm. An estimate of optical band gap is obtained by analyzing $(\alpha h\nu)^2 \sim h\nu$ curve based on the relationship $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where A is a constant and n depends on the nature of the transition ($n = 1$ for direct allowed transition). The E_g for direct transition is estimated from the intercept of the straight line on the energy ($h\nu$) axis. The band gap of sample 1 is estimated to be 2.13 eV, which blue-shifts by ≈ 0.9 eV compared with that of the bulk (1.2 eV) due to quantum size effect.

In summary, we have successfully synthesized CuO nanoleaves by the microwave-assisted aqueous solution method. This method is a fast, simple, seedless and template-free route for production of CuO nanoleaves. CuO nanoleaves have lateral sizes from hundreds nm to several µm and average thickness of ≈ 10 nm. The band gap of CuO nanoleaves was estimated to be 2.13 eV, which shows significant blue-shift compared with that of the bulk.

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